

## 3.0 Methods, Issues, and Criteria for Measuring $K_d$ Values

### 3.1 Introduction

The partition (or distribution) coefficient,  $K_d$ ,<sup>1</sup> is a measure of sorption of contaminants to soils and is defined as the ratio of the quantity of the adsorbate adsorbed per unit mass of solid to the amount of the adsorbate remaining in solution at equilibrium. It is the simplest, yet least robust model available. There are 5 general methods used to measure  $K_d$  values: laboratory batch method, *in-situ* batch method, laboratory flow-through (or column) method, field modeling method, and  $K_{oc}$  method. Each method has advantages and disadvantages, and perhaps more importantly, each method has its own set of assumptions for calculating  $K_d$  values from experimental data. Consequently, it is not only common, but expected that  $K_d$  values measured by different methods will produce different values.

A number of issues exist concerning the measurement of  $K_d$  values and the selection of  $K_d$  values from the literature. These issues include: using simple versus complex natural geologic materials as adsorbents, field variability, the “gravel issue,” the “colloid issue,” and the particle concentration effect. Soils are a complex mixture containing solid, gaseous, and liquid phases. Each phase contains several different constituents. The use of simplified systems containing single mineral phases and aqueous phases with 1 or 2 dissolved species have provided valuable paradigms for understanding sorption processes in more complex, natural systems. However, the  $K_d$  values generated from these simple systems are generally of little value for importing directly into transport models. Values for transport models should be generated from materials from or similar to the study site. The “gravel issue” is the problem that transport modelers face when converting laboratory-derived  $K_d$  values based on experiments using the less than 2-mm fraction into values that can be used in systems containing particles greater than 2 mm in size. No standard methods exist to address this issue. The “colloid issue” was discussed previously in Section 2.7. Some investigators have observed that  $K_d$  values determined in the laboratory often decrease as the ratio of solid to solution used in the measurements increases. This particle concentration effect is puzzling, because a  $K_d$  value should not depend from a theoretical perspective on the solid-to-solution ratio. Investigators have offered several explanations involving physical/chemical processes and/or experimental artifacts for the observed dependency.

Spatial variability provides additional complexity to understanding and modeling contaminant retention to subsurface soils. The extent to which contaminants partition to soils often changes as field mineralogy and chemistry changes. Thus, a single  $K_d$  values is often not sufficient for an entire study site and should change as important environmental conditions change. It is therefore important to be able to identify and measure the effect of ancillary environmental parameters that influence contaminant sorption. Three approaches used to vary  $K_d$  values in transport codes are the  $K_d$  look-up table approach, the parametric  $K_d$  approach, and the mechanistic  $K_d$  approach.

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<sup>1</sup> A list of acronyms, abbreviations, symbols, and notation is given in Appendix A. A list of definitions is given in Appendix B

The extent to which these approaches are presently used and the ease of incorporating them into flow models varies greatly.

The objective of this chapter is to provide an overview of the different methods of measuring and determining  $K_d$  values used in site-specific contaminant transport and risk assessment calculations. Issues regarding the selection of  $K_d$  values from the literature for use in screening calculations are discussed.

### 3.2 Methods for Determining $K_d$ Values

There are 5 methods of determining  $K_d$  values: (1) laboratory batch method, (2) *in-situ* batch method, (3) laboratory flow-through (or column) method, (4) field modeling method, and (5)  $K_{oc}$  method (EPA, 1991; Ivanovich *et al.*, 1992; Jackson and Inch, 1989; Johnson *et al.*, 1995; Karickhoff *et al.*, 1979; Landstrom *et al.*, 1982; Lyman *et al.*, 1982; Roy *et al.*, 1991; Serkiz *et al.*, 1994; Sposito, 1984; van Genuchten and Wierenga, 1986). Each method provides an estimate of the propensity of a contaminant to sorb to the solid phase. However, the techniques used and the assumptions underlying each method are quite different. Consequently,  $K_d$  values for a given system that were measured by different methods commonly have values ranging over an order of magnitude (Gee and Campbell, 1980; Relyea, 1982). This subsection will describe the different methods and compare their implicit and explicit assumptions.

The  $K_d$  model originates from thermodynamic chemistry (see detailed discussion in Chapter 2) (Alberty, 1987). It is a measure of sorption and is defined as the ratio of the quantity of the adsorbate adsorbed per gram of solid to the amount of the adsorbate remaining in solution at equilibrium. For the reaction



the mass action expression is the partition coefficient ( $K_d$ , ml/g):

$$K_d = \frac{A_i}{C_i} \quad (3.2)$$

where  $A$  = concentration of free or unoccupied surface adsorption site on a solid phase (mol/ml),  
 $C_i$  = total dissolved adsorbate concentration remaining in solution at equilibrium (mol/ml or  $\mu\text{g/ml}$ ), and  
 $A_i$  = concentration of adsorbate on the solid at equilibrium (mol/g or  $\mu\text{g/g}$ ).

Equation 3.2 is valid only when  $A$  is in great excess with respect to  $C_i$  and the activity of  $A_i$  is equal to unity. For saturated conditions and non-polar organic constituents, sorption from the aqueous phase to the porous media of the subsurface can be treated as an equilibrium-partitioning

process when solute concentrations are low (*e.g.*, either  $\leq 10^{-5}$  molar, or less than half the solubility, whichever is lower) (EPA, 1989). Partitioning often can be described using the above linear isotherm.

Also inherent in the thermodynamic definition of the  $K_d$  term are the assumptions that the reaction is independent of the contaminant concentration in the aqueous phase and that the system is reversible, *i.e.*, that the desorption rate is equal to the adsorption rate. The thermodynamic  $K_d$  term describes a precisely defined system, including fixed pH and temperature, with one type of adsorption site,  $A$ , and one type of dissolved aqueous species,  $C_i$ . Although the thermodynamic  $K_d$  term is overly restrictive for use in natural heterogeneous systems, it provides an important paradigm to base empiricised  $K_d$  terms. The assumptions that need to be made to empiricise this construct vary between analytical methods.

### 3.2.1 Laboratory Batch Method

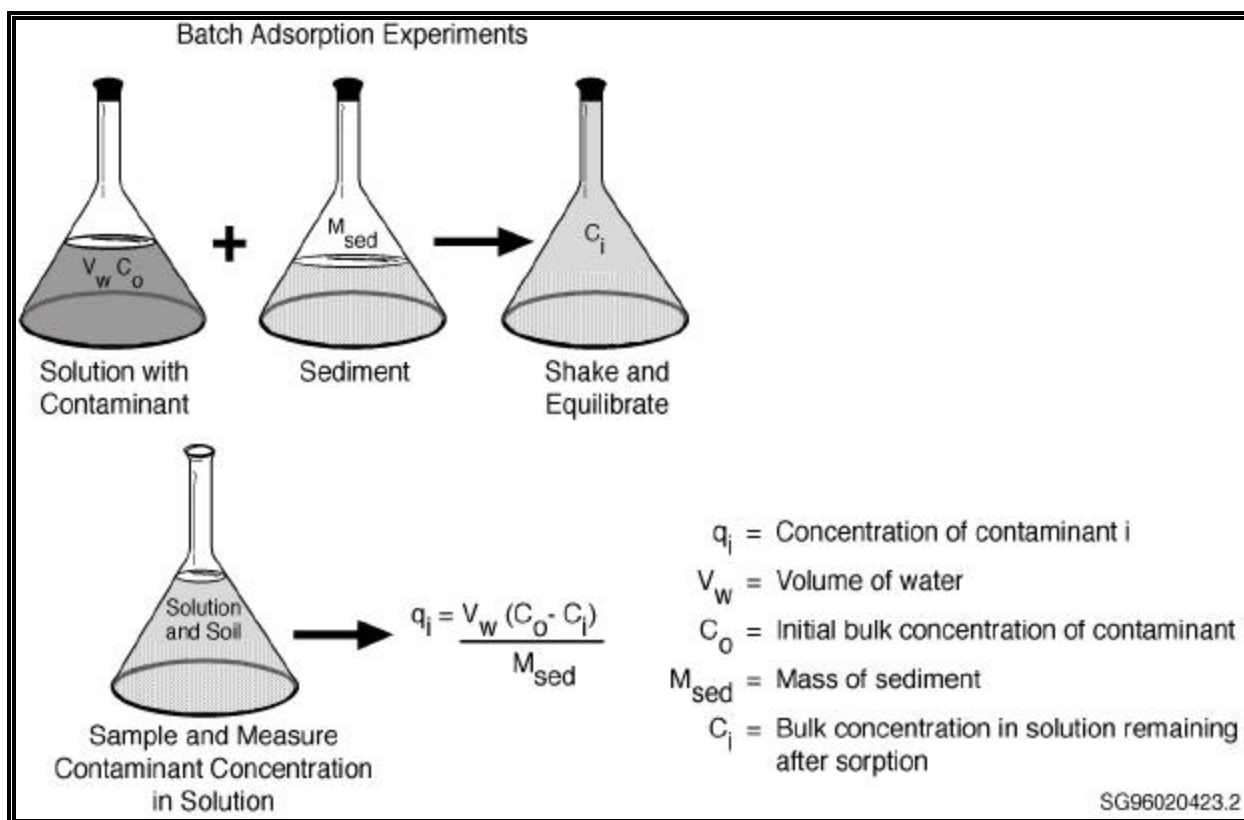
Batch studies represent the most common laboratory method for determining  $K_d$  values (ASTM, 1987; EPA, 1991; Roy *et al.*, 1991). Figure 3.1 illustrates an EPA (1991) procedure for measuring a batch  $K_d$  value. A well characterized soil of known mass ( $M_{sed}$ ) is added to a beaker. A known volume ( $V_w$ ) and concentration ( $C_0$ ) of an aqueous contaminant solution is added to the soil in the beaker. The beaker is sealed and mixed until sorption is estimated to be complete, typically 1 to 7 days. When possible, the person conducting the study should ascertain the actual time required to reach sorption equilibrium. The solutions are centrifuged or filtered, and the remaining concentration of the contaminant ( $C_i$ ) in the supernatant is measured. The concentration of adsorbate sorbed on the solid phase ( $A_i$ , sometimes noted as  $q_i$ ) is then calculated by Equation 3.3:

$$A_i = q_i = \frac{V_w (C_0 - C_i)}{M_{sed}} \quad (3.3)$$

Equation 3.3 is used to calculate the numerator of the  $K_d$  term (Equation 3.2) and the denominator,  $C_i$ , of the  $K_d$  term is measured directly in the laboratory. Thus,

$$K_d = \frac{V_w (C_0 - C_i)}{M_{sed} C_i} \quad (3.4)$$

For organic compounds that can degrade into other compounds, it should be noted that the difference in solution concentrations in Equation 3.3 represents both adsorption and degradation. Therefore, the calculated  $K_d$  for organic compounds of this type can overestimate the amount of true adsorption. If container blanks are not included in the batch test matrix, adsorption of a contaminant to the container is included in the calculated  $K_d$ . Care must be taken when interpreting batch  $K_d$  test results.



**Figure 3.1.** Procedure for measuring a batch  $K_d$  value (EPA, 1991).

It is important to note that the interpretation of results from batch  $K_d$  sorption tests generally allow no distinction to be made on how the sorbate (*i.e.*, contaminant) is associated with the sorbent (*i.e.*, soil). The sorbate may be truly adsorbed by ion exchange, chemisorption, bound to complexes that are themselves sorbed on the solid, and/or precipitated. If the  $K_d$  values are going to be used in transport calculations that already account for precipitation processes, it is imperative that the  $K_d$  values only include the decrease in dissolved concentrations of the sorbate due to adsorption. That is, the user must be certain that the experiments were performed correctly to prevent significant removal of the sorbate by precipitation reactions. Otherwise, the estimated retardation can be significantly overestimated.

There are several variations of this general procedure, each variation addressing the specific needs of the system. It is necessary to have some latitude in the method because of limits due to analytical chemistry considerations. For instance, for contaminants in which very low sorption is expected, a larger ratio of solid to liquid may increase the small difference in the term  $(C_0 - C_i)$ . Conversely, for contaminants in which high sorption is expected, a lower ratio of solid to liquid may be desirable. For gamma-ray emitting contaminants, it is possible to directly count the

activity on the equilibrated solid and in the solution, such that the  $K_d$  can be directly determined as opposed to relying on the difference in activity (*i.e.*, concentration) in the solution phase only.

One of the most common variations of the EPA method is to conduct a series of batch tests that are identical except for varying of the concentration of the dissolved contaminant,  $C_i$ . The  $K_d$  for the resulting isotherm is typically calculated from the slope of a  $C_i$  versus  $A_i$  plot. As discussed in Section 2.3.3, adsorption isotherm experiments are often conducted to evaluate the effect of contaminant concentration on adsorption, while other parameters are held constant. For soils, it is common knowledge that contaminant adsorption can deviate from the linear relationship required by the  $K_d$  construct. This approach obviously requires more work, but can provide a more accurate estimate.

Other variations of the batch  $K_d$  procedure deal with the ratio of solids to liquid, liquid composition, and contaminant concentration. A detailed description of a batch  $K_d$  procedure is included in Appendix C.

Contaminant transport modelers are often interested in the  $K_d$  value of a contaminant in a specific groundwater plume (*e.g.*, an acidic plume) in contact with a specific soil. In such a case, an experimenter would spike the contaminant into a representative groundwater, as opposed to pure water. Additionally, the experimenter would attempt to equilibrate the soils with the background aqueous solution (*e.g.*, the acidified groundwater) before bringing the soil in contact with the contaminant of interest. The reason for this latter step is to isolate the adsorption/desorption reaction of interest between the contaminant and soil. By pre-equilibrating the soil first with the acidic plume water (without the contaminants present), all the extraneous chemical reactions should be near equilibrium. Then, when the contaminant is added, its reaction is isolated.

The batch method is popular because the equipment, cost, and time requirements are low and the methodology is quite simple. However, the seemingly elementary operations mask numerous subtleties resulting in variability of data (EPA, 1991; Roy *et al.*, 1991; Serne and Relyea, 1981). One of the most comprehensive exercises to evaluate interlaboratory precision and identify important procedural details was conducted by 9 laboratories (Serne and Relyea, 1981). General guidelines on groundwater compositions, radionuclides, and procedural details were given to participants in this exercise. The measured  $K_d$  values were surprisingly varied for 2 of 3 contaminants investigated. As much as 3 orders of magnitude difference were determined in cesium ( $1.3 \pm 0.4$  to  $880 \pm 160$  ml/g) and plutonium ( $70 \pm 36$  to  $63,000 \pm 19,000$  ml/g). Conversely, the strontium  $K_d$  values measured in the 9 laboratories were within an order of magnitude of each other,  $1.4 \pm 0.2$  to  $14.9 \pm 4.6$  ml/g. Serne and Relyea (1981) concluded that the cause of the variability of the plutonium and cesium  $K_d$  values was due to: (1) method of tracer addition to solution, (2) solution-to-solid ratio, (3) initial tracer concentration in influent solution, (4) particle size distribution, (5) solid-solution separation method, (6) sample containers, and (7) temperature. The authors discussed in detail each of these parameters that are generally not controlled in batch  $K_d$  methods.

Essentially all of the assumptions associated with the thermodynamic  $K_d$  value (Equation 3.2) are violated in the common batch  $K_d$  value. The natural soils used in these studies are not completely defined or quantified with respect to their mineralogy and organic phases. The background aqueous phases that are spiked with the adsorbate are typically not pure water and are rarely completely characterized, especially in the case when natural groundwater are used as the background aqueous phase. The background aqueous phases often contain the dominant electrolytes of the study site or actual uncontaminated groundwater from the study site, consisting of several dissolved and perhaps colloidal species. Furthermore, the sorption/desorption process of adsorbates from soils is typically not reversible, *i.e.*, hysteresis is observed, such that desorption occurs at a slower rate than sorption (Sposito, 1994). However, the batch  $K_d$  term can be of much greater value to the contaminant transport modeler than the thermodynamic value if the soil and the aqueous phase closely represent the natural system being modeled. Importantly, such a complex system, though not completely characterized, provides the best available estimate of the extent to which a sorbate partitions to a given soil in the presence of the electrolytes present in the experiment. This issue of measuring  $K_d$  values in complex- versus simple-systems is further discussed in Section 3.3.1.

One significant limitation inherent in the batch method is that commonly used analytical instruments can not differentiate between species of a given contaminant. For example, the atomic absorption (AA) spectrophotometer can measure total cadmium in the aqueous phase but can not identify each of its species [*e.g.*,  $\text{Cd}^{2+}$ ,  $\text{CdSO}_4^{\text{aq}}$ ,  $\text{CdCl}^-$ , *etc.*]. Multiple species typically exist in groundwater and the effect of their individual  $K_d$  values have a profound effect on the overall  $K_d$  value. For example, consider a system that consists of a contaminant or radionuclide with 2 equal concentration species that are kinetically slow at converting between each composition state; one with a  $K_d$  of 0 ml/g and the second with a  $K_d$  of 1,000 ml/g. The laboratory batch method would yield an intermediate  $K_d$  of about 30 ml/g in an experiment with a solution-to-solid ratio of 30. A demonstration calculation illustrating this issue is given in Figure 3.2. Using the  $K_d$  value 30 ml/g in subsequent mass transport calculations would not be conservative because 50 percent of the radionuclide would move at the speed of the carrier solution. For this reason, when there is any suspicion that multiple species with significantly differing  $K_d$  values may be present, a second sorption methodology, such as the flow-through method (Section 3.2.3), should be run to search for early breakthrough.

**Assumptions:**

- Total concentration,  $C_0$ , of contaminant I in the original solution is 1,000 mg/ml.
- Batch test is performed with 1 g of clay soil contacting 30 ml of the original solution.
- The total concentration  $C_0$  is equally divided between two species, A and B, of contaminant I.
- The true  $K_d$  values for species A and B are 0 and 1,000 ml/g, respectively.
- Kinetic barriers exist that affect their interconversion between these two composition states over the time period of the test.

**Equations and Calculation:**

Rearranging the equation

$$K_d = \frac{V_w (C_0 - C_i)}{M_{sed} C_i}$$

to solve for the concentration of species X of contaminant I ( $C_{Xi}$ ) (*i.e.*,  $C_{Ai}$  and  $C_{Bi}$ , where  $C_A$  and  $C_B$  at end of test), one gets

$$C_{Xi} = \frac{C_{0,X} V_w}{K_{d,X} M_{sed} + V_w}$$

For  $C_{Ai}$ , we know that there is no adsorption. Therefore,  $C_{Ai} = C_{0,A} = 0.5 \cdot C_0 = 500$  mg/ml.

For  $C_{Bi}$ , we calculate from the above equation for  $C_{Xi}$ :

$$C_{Bi} = \frac{500 \times 30}{(1,000 \times 1) + 30} = \frac{15,000}{1,030} = 14.56$$

$C_i$  for total solution is

$$C_{Ai} + C_{Bi} = 500 + 14.56 = 514.56$$

Therefore, if one does not realize that multiple contaminant species are present which do not rapidly interconvert, the overall  $K_d$  for the total contaminant would be

$$K_d = \left( \frac{1,000 - 514.56}{514.56} \right) \frac{30}{1} = 28.30 \approx 28$$

**Figure 3.2.** Demonstration calculation showing affect on overall  $K_d$  by multiple species that have different individual  $K_d$  values and are kinetically slow at interconverting between each composition state.

### 3.2.2 *In-situ Batch Method*

A method developed out of the desire to produce an *in-situ*  $K_d$  value has been used to a limited extent (Jackson and Inch, 1989; Johnson *et al.*, 1995; Landstrom *et al.*, 1982; McKinley and Alexander, 1993; Read *et al.*, 1991). The procedure used in this method is somewhat similar to that of the laboratory batch  $K_d$  method described in Section 3.2.1. A core sample containing a paired solid and aqueous phase is removed directly from an aquifer. The aqueous phase is separated from the solid phase by centrifugation or filtration and then analyzed for the solute concentration,  $C_i$ . The solid is then analyzed for the concentration of the contaminant associated with the solid phase,  $A_i$ .

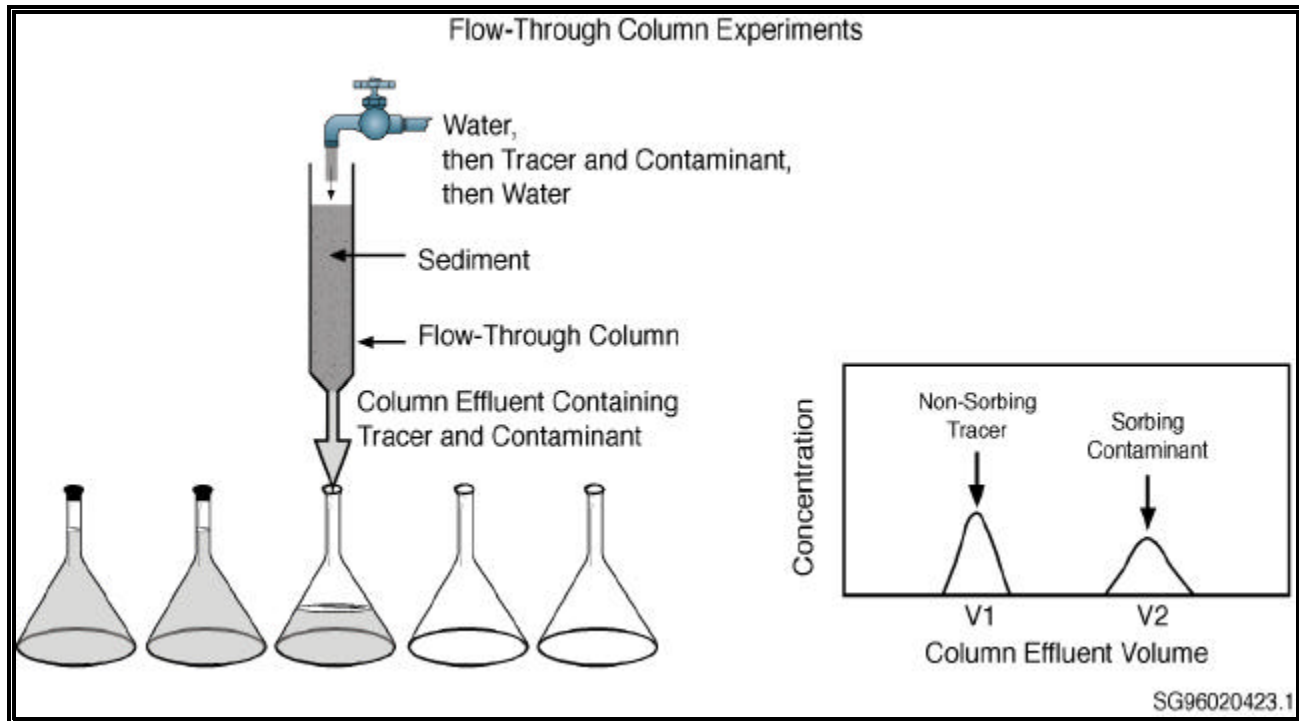
Clearly, the advantage of this approach compared to the laboratory  $K_d$  method is that the precise solution chemistry and solid phase mineralogy is used for the modeling. Furthermore, the pore water removed from the core material may have had sufficient time to equilibrate and therefore true equilibrium may be attained. The disadvantages are somewhat less apparent but none the less appreciable. The concentration of most metal contaminants on the soil surfaces is typically quite low, in the mg/kg range. It should be noted moreover that the minimum detection limit for radionuclides on solid surfaces is even lower. The most common instruments available to measure metal concentrations on surfaces, energy dispersive x-ray analysis (EDX), or x-ray fluorescence, typically has detection limits in the order of 10,000 and 100 mg/kg, respectively. Another method of measuring  $A_i$  is to dissolve the solid phase with acid and then measure the resulting solution by inductively coupled plasma spectroscopy (ICP), inductively coupled plasma/mass spectroscopy (ICP/MS), and/or atomic adsorption spectroscopy (AA) techniques. This latter technique may provide a lower (*i.e.*, better) detection limit. In addition to the detection limit problem, it is not possible by any of these methods to distinguish between sorption and precipitation - processes which are treated quite differently in transport models. Furthermore, some trace metals are present in crystalline lattice sites of minerals present in soils. These molecules are not readily controlled by adsorption/desorption and should not be included in the  $q_i$  term. An in-depth discussion of the limitations of the *in-situ* batch method is presented by McKinley and Alexander (1993). For anthropogenic radionuclides present at trace levels, it is possible to assume that precipitation and lattice site contributions are nil and that the total mass/activity measured on the solid does represent adsorption/desorption-controlled molecules. In this scenario, a field *in-situ*  $K_d$  may be accurate.

One rather successful application of this technique was recently reported by Johnson *et al.* (1995). They compared laboratory and field batch  $K_d$  values of uranium along a transect through a pH gradient of pH 3.0 to 5.6. The field results yielded  $K_d$  values that ranged from 0.4 to greater than 15,000 ml/g for approximately 36 samples. The  $K_d$  values generated by the laboratory batch technique were generally lower, ranging from 0.08 to greater than 10,000 ml/g. The  $K_d$  values determined by both methods varied as a function of soil pH at the study site. When both sets of values were incorporated into a transport code, the results were not significantly different, *i.e.*, both methods were essentially equally good at predicting contaminant retardation in the study site.



### 3.2.3 Laboratory Flow-Through Method

The laboratory flow-through (or column) method of determining  $K_d$  values is the second most commonly used method (EPA, 1991; Relyea, 1982; Van Genuchten and Wierenga, 1986). A solution containing known amounts of a contaminant is introduced into a column of packed soil of known bulk density (*i.e.*, mass of soil per unit volume of column, g/ml) and porosity (*i.e.*, volume of pore space per unit volume of column, ml/ml) (Figure 3.3). The effluent concentration is monitored as a function of time. A known amount of a nonadsorbing tracer may also be introduced into the column and its time-varying concentration provides information about the pore-water velocity. The resulting data is plotted as a break-through curve (Figure 3.3). The velocity of each constituent (*i.e.*, tracer and contaminant) is calculated as the length of the column divided by the constituent's mean residence time.



**Figure 3.3.** Procedure for measuring a column  $K_d$  value.

The mean residence time for a pulse input is calculated as follows (Relyea, 1982):

$$t_{\text{pulse}} = \frac{\int_{t_{\text{min}}}^{t_{\text{max}}} t C_i dt}{\int_{t_{\text{min}}}^{t_{\text{max}}} C_i dt} \quad (3.5)$$

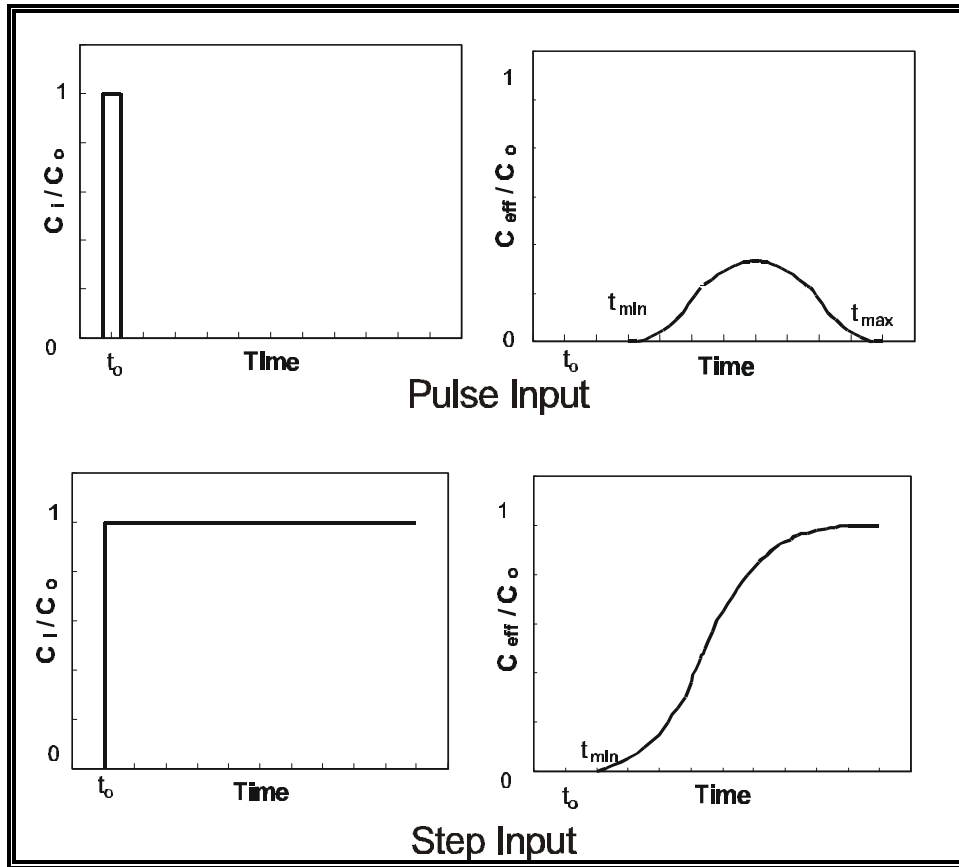
where  $t_{\text{pulse}}$  = mean residence time for a pulse input (hr),  $t_{\text{max}}$  is the end of the break-through curve (hr),  
 $t_{\text{min}}$  = beginning of the break-through curve (hr),  
 $C_i$  = constituent concentration [(g or curies)/ml], and  
 $t$  = time (hr).

The relative concentrations of a constituent at the input source and in the effluent based on a pulse input are shown schematically in the top left and right of Figure 3.4. The mean residence time for a step (continual steady-state) input is calculated as follows:

$$t_{\text{step}} = \frac{\int_{C_{\text{min}}}^{C_{\text{max}}} t dC}{\int_{C_{\text{min}}}^{C_{\text{max}}} C_i dt} \quad (3.6)$$

where  $t_{\text{step}}$  = mean residence time for a step input/release (hr),  
 $C_{\text{max}}$  = maximum concentration measured in the effluent [(g or curies)/ml], and  
 $C_{\text{min}}$  = minimum concentration measured at the beginning of breakthrough [(g or curies)/ml].

When the effluent curve is ideal,  $t_{\text{step}}$  equals the time when the breakthrough curve reaches 0.5 or 50 percent breakthrough (*i.e.*,  $C_i/C_o=0.5$ ). The relative concentrations of a constituent at the input source and in the effluent based on a step input are shown schematically in the bottom left and right of Figure 3.4.



**Figure 3.4.** Schematic diagram showing the relative concentrations of a constituent at the input source (figures on left) and in the effluent (figures on right) as a function of time for a pulse versus step input. [ $C_o$ ,  $C_i$ , and  $C_{eff}$  refer, respectively, to the concentration of the constituent at  $t_o$  and the concentrations of the constituents in the input and effluent.]

The retardation factor ( $R_f$ ) is the ratio of the pore-water velocity ( $v_p$ , cm/hr) to the contaminant velocity ( $v_c$ , cm/hr):

$$R_f = \frac{v_p}{v_c} \quad (3.7)$$

The pore-water velocity is operationally defined as the velocity of the nonadsorbing tracer.

The  $K_d$  value can be calculated directly from the retardation factor ( $R_f$ ) and soil properties. Depending upon the environmental conditions in which the contaminant moves and interacts with the soil, the retardation factor can be correlated to the partition coefficient in a number of different ways. At least 4 formulations of the retardation factor have been proposed [see reviews in Bouwer (1991) and Whelan *et al.* (1987, 1996)]. These include the following:

$$R_f = \frac{n}{n_e} + \frac{K_d \rho_b}{n_e} \quad (3.8)$$

$$R_f = 1 + \frac{K_d \rho_b}{n_e} \quad (3.9)$$

$$R_f = 1 + \frac{K_d \rho_b}{n} \quad (3.10)$$

$$R_f = 1 + \frac{K_d \rho_b}{\theta} \quad (3.11)$$

where  $n$  = total porosity ( $\text{cm}^3$  pore/ $\text{cm}^3$  total volume),  
 $n_e$  = effective porosity ( $\text{cm}^3$  pore/ $\text{cm}^3$  total volume),  
 $\theta$  = volumetric water content in the vadose zone ( $\text{cm}^3$  water/ $\text{cm}^3$  total volume), and  
 $\rho_b$  = bulk density (g soil/ $\text{cm}^3$  total volume).

Total porosity is the ratio of the air/water volume to the total soil. The effective porosity differs from the total porosity in that the numerator is the volume of only those pore spaces that water can travel through, excluding such void volumes as exist within aggregates or dead-end pore spaces. Equation 3.10 was the original equation relating  $K_d$  to  $R_f$ . It was developed on an empirical basis for use in chemical engineering and was first applied to groundwater situations by Higgins (1959) and Baetslé (1967). Equations 3.8-3.11 were derived from the general transport equation, which is the differential equation describing solute concentration changes in relation to time, distance, dispersion coefficient, water velocity, soil bulk density, porosity, mass of solute per unit dry mass of soil, and degradation of solute (Bouwer, 1991).

Equation 3.8 assumes that the soil has 2 types of pore spaces, those that permit flow to occur ( $n_e$ ), and those pore spaces that do not permit flow to occur ( $n - n_e$ ). The contaminant in Equation 3.8 is assumed to migrate through the interconnected pore spaces, diffuse into dead-end pore spaces, and instantaneously adsorb to or desorb from the soil matrix where fluid is and is not flowing. Equation 3.8 also assumes that the solute concentration in the dead-end pore spaces is equivalent to the solute concentration in the free-flowing spaces. Equation 3.8 has the appearance of being more comprehensive than the other equations, but it does not allow the contaminant to travel with the same speed as the fluid (*i.e.*, nonadsorbing case), unless the total and effective porosities are equal. Experience has shown that Equation 3.8 does not adequately reflect real-world phenomena, suggesting deficiencies in our understanding of the geohydrochemical processes

impacting contaminant movement in the subsurface environment (Whelan *et al.*, 1987). Furthermore, in field studies, total porosity ( $n$ ) can be measured directly, whereas effective porosity ( $n_e$ ) can only be calculated from equations based on assumptions that are difficult to defend (Freeze and Cherry, 1979).

Equation 3.9 includes the same processes as Equation 3.8, except that the contaminant does not diffuse into the dead-end pore spaces. Many models use Equation 3.9 in their formulations. van Genuchten and Wierenga (1986) suggest the use of Equation 3.10. Equation 3.10 includes the same phenomena as Equation 3.9 except that the porous medium contains no dead-end pore spaces. Again, the merit of its use over Equation 3.9 is that the measurable parameter  $n$  is included in the formulation and not the calculated parameter  $n_e$ . Equation 3.8, 3.9, and 3.10 describe chemical retardation in the saturated zone, whereas Equation 3.11 describes chemical retardation in the unsaturated, or vadose, zone. As with Equation 3.10, contaminant transport and retardation in Equation 3.11 occurs only in the free-flowing pore space. Bouwer (1991) promotes the use of Equation 3.11 but defines the  $\theta$  term more generally as the water that is moving, whether in unsaturated or saturated conditions. In his derivation of Equation 3.11, Bouwer suggests that the  $\theta$  term also be used to quantify the mobile phases of water. Along with van Genuchten and Wierenga (1986), he also contends that the use of Equation 3.11 allows better distinction between retardation effects due to sorption and acceleration effects due to preferential flow or anion exclusion.

Flow-through column experiments are appealing in that they allow observation of contaminant migration rates in the presence of hydrodynamic effects (*e.g.*, dispersion, colloidal transport, *etc.*), and chemical phenomena (*e.g.*, multiple species, reversibility, *etc.*). Ideally, flow-through column experiments would be used exclusively for determining  $K_d$  values, but equipment costs, time constraints, experimental complexity, and data reduction uncertainties discourage widespread use. One common problem in using column studies to measure  $K_d$  values is that the breakthrough curves are asymmetric. Such curves cannot be interpreted using Equations 3.8, 3.9, 3.10, or 3.11. They require more complicated equations for solving for  $K_d$  (Brusseau and Rao, 1989; van Genuchten and Alves, 1982; van Genuchten and Wierenga, 1986).

One of the unique characteristics of measuring  $K_d$  values from column experiments is that nonequilibrium conditions can be imposed. Especially under conditions in which the solute has slow adsorption kinetics [*e.g.*, those that may occur with uranium (Sposito, 1994)] or when groundwater flow is fast, a measure of adsorption at equilibrium may over-estimate the extent to which sorption occurs under actual field conditions. When either of these conditions are known to exist in a study site, researchers should conduct column experiments at the flow rate existing in the field, thereby creating realistic conditions.

Relyea (1982) provided an excellent review on the theoretical and experimental application of the laboratory flow-through method of determining  $K_d$  values. He reported that retardation factors measured in column experiments depended on the water velocity and column dimension. For short columns and slow water velocities, diffusion can become a major transport mechanism

resulting in lower retardation factors and lower  $K_d$  values. At high velocities the effective pore volume of a sample can decrease for short columns. High water velocities can also result in lower retardation factors as a result of the solute not having sufficient time to adsorb to the soil, *i.e.*, chemical equilibrium was not obtained. The effects of column length, mass of solute added to column, diameter ratio of particle to column, and ratio of column diameter to column width on the measured  $K_d$  value were also presented by Relyea (1982).

### 3.2.4 Field Modeling Method

Field studies can provide accurate indications of the time of travel of the contaminant because the concentrations of a dissolved contaminant are measured directly from samples taken from monitoring wells. The field modeling method of estimating a  $K_d$  value, also called the field calibration method, uses a transport model and existing groundwater monitoring data. This process, which is referred to as calibrating a groundwater transport model to  $K_d$  values, involves treating the  $K_d$  value as an adjustable parameter (or dependent variable) while simulating contaminant concentrations determined at monitoring wells. Groundwater calibration captures the essence of the problem in the field. This is an iterative process that frequently requires the adjusting the values for several other input parameters, such as effective porosity, dispersion, and flow rate, to yield meaningful  $K_d$  values. The minimum information that is needed for such a calculation is the contaminant concentration at the source term, date of release, groundwater flow path, groundwater flow rate, contaminant concentration at a monitoring well, distance between source-release and monitoring well, dispersion coefficient, and source term. The retardation of the chemical is then estimated as the ratio of the pore-water velocity to the contaminant velocity (Equation 3.7). The pore-water velocity,  $v_p$ , can be based on Darcy's law (Freeze and Cherry, 1979) where

$$v_p = \frac{v_d}{n_e} \quad (3.12)$$

where  $v_d$  = Darcy velocity  
 $n_e$  = effective porosity

However, 2 key drawbacks to this technique is that it is highly site specific and very model dependent. Additionally, many assumptions have to be made about the water flow in the study site including uniform flow and flow path. Not obvious, is that the  $K_d$  value calculated by this method greatly improves with more data. A detailed description of the theory of calculating  $K_d$  values by this method and some examples of this approach are presented in Chapter 4.

### 3.2.5 $K_{oc}$ Method

The extent to which an organic contaminant partitions between the solid and solution phases is determined by several physical and chemical properties of the contaminant and soil (Lyman *et al.*, 1982). Since most sorption of hydrophobic organic substances is to the natural organic matter present in sediments or soils, the usual approach is to assume that all sorption is to that matter and

to invoke a partition coefficient between organic carbon ( $K_{oc}$ ) or organic matter ( $K_{om}$ ) and water (Seth *et al.*, 1999). Hydrophobic solutes appear to bind readily and rapidly with the outer surface region in a few hours to a few days and then diffuse slowly into (and out of) the hydrophobic interior region and narrow cavities in the sediment or soil organic matter during time periods of weeks (Seth *et al.*, 1999). An empirical approach that has had wide acceptance in the scientific community is the organic-carbon partitioning coefficient ( $K_{oc}$ ) method introduced by Karickhoff *et al.* (1979).

For this method, sorption of an organic contaminant, such as polynuclear aromatic hydrocarbon (PAH), is assumed to occur only to the organic material in the soil. The partitioning between the solid and solution phases is expressed as:

$$K_d = K_{oc} f_{oc} \quad (3.13)$$

where  $K_{oc}$  = ratio of the contaminant concentration on the organic matter on a dry weight basis to its dissolved concentration in the surrounding fluid (ml/g) and  
 $f_{oc}$  = fraction of organic carbon in the soil (mg/mg).

Importantly, the  $K_{oc}$  method is only applicable for estimating organic compound partitioning. Gschwend and Wu (1985) report that if precautions are taken to eliminate or account for nonsettling microparticles or organic macromolecules which remain in the aqueous phase during laboratory sorption tests, the observed organic-carbon partitioning coefficient have been found to remain constant over a wide range of environmental and experimental conditions. However, recent studies by Chiou *et al.* (1998) and Seth *et al.* (1999) indicate that for any given chemical, an inherent variability in  $K_{oc}$  values is expected as a result of different environmental conditions and equilibrium times. Dragun (1988) identified the following conditions when this approach is less accurate:

- When the organic fraction,  $f_{oc}$ , is less than 1.0 percent<sup>1</sup> (LaGrega, 1994) or greater than 20 percent (EPA, 1988)
- When there are large amounts of swelling clays present (*e.g.*, montmorillonite)
- When the partitioning organic compound is polar
- When mechanisms other than simple partitioning contribute to adsorption (*e.g.*, cation-exchange, anion-exchange)
- When a substantial time is required to reach equilibrium

The organic content of most soils falls in the range of 0.2 to 3.0% (LaGrega, 1994).

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<sup>1</sup> Other limits have been suggested for the minimum organic fraction,  $f_{oc}$ , such as less than 0.1 percent (EPA, 1989) or less than a few tenths of a percent (Pignatello, 1989).

The commonest correlation for  $K_{oc}$  is with the octanol-water partition coefficient ( $K_{ow}$ ) for which extensive databases and reliable estimation methods exist (Seth *et al.*, 1999). A simplified relationship between these two parameter is given by Equation 3.14.

$$K_{oc} = \alpha K_{ow} \quad (3.14)$$

where  $\alpha$  = correlation coefficient (unitless).

LaGrega (1994) reports a value of ( $\alpha = 0.63$ ) as a commonly used value while Seth *et al.* (1999) calculate a value of ( $\alpha = 0.35$ ) with a variation in  $\alpha$  by a factor of 2.5 in either direction. Seth *et al.* (1999) also suggested that  $K_{oc}$  estimates be viewed as a distribution, which includes uncertainties about attainment of equilibrium and the variability in the composition of organic matter present in soils and sediments, rather than as a single point value.

Streng and Peterson (1989) applied the principle of the  $K_{oc}$  model to estimating the partition coefficients for organic compounds on soils. They defined the  $K_d$  for organic compounds through the combination of the  $K_{oc}$  model and a parametric model (discussed in Section 3.4.2) based on the concentrations of organic material ( $C_{om}$ , percent w/w), clay ( $C_{clay}$ , percent w/w), silt ( $C_{silt}$ , percent w/w) and sand ( $C_{sand}$ , percent w/w) as dependent variables:

$$K_d = 10^{-4} K_{oc} [57.735(C_{om}) + 2.0(C_{clay}) + 0.4(C_{silt}) + 0.005(C_{sand})] \quad (3.15)$$

Equation 3.15 has the disadvantage of requiring more input parameters than Equations 3.13 and 3.14, but it provides an innovative approach for estimating the  $K_d$  of organic compounds.

### 3.3 Issues Regarding Measuring and Selecting $K_d$ Values

#### 3.3.1 Using Simple Versus Complex Systems to Measure $K_d$ Values

Soils are a complex mixture of solid, gaseous, and liquid phases. Each phase contains several different constituents. Sposito (1989) estimated that the aqueous phase of a typical soil easily contains between 100 and 200 different soluble complexes, many of them involving metal cations and organic ligands (Table 3.1). The main effect of pH on these complexes, as is evident in Table 3.1, is to favor free metal cations and protonated anions at low pH and carbonate or hydroxyl complexes at high pH. The number of soluble complexes are also likely to be greater in systems with elevated pH and organic matter concentrations. The solid phase in natural soils typically contains more than 10 different constituents, including minerals, microbes, oxides, naturally occurring organic matter, and organic, carbonate and/or oxide (e.g., iron, aluminum, and manganese) coatings. The gas phase is quite different from that of above ground air as a result of its interaction with the other phases and effects of pressure, temperatures, and microbial activity (Sposito, 1989). For instance, the carbon dioxide levels is commonly several orders of magnitude greater in soils than in above ground air (Wood and Petratis, 1984).



**Table 3.1.** Representative chemical species in acidic and basic soil solutions (after Sposito, 1989).

Cation	Principal Species <sup>1</sup>	
	Acid Soils	Alkaline Soils
Aluminum	Al-org, <sup>2</sup> AlF <sup>2+</sup> , AlOH <sup>2+</sup>	Al(OH) <sub>4</sub> <sup>-</sup> , Al-org
Cadmium	Cd <sup>2+</sup> , CdSO <sub>4</sub> <sup>°</sup> (aq), CdCl <sup>+</sup>	Cd <sup>2+</sup> , CdCl <sup>+</sup> , Cd SO <sub>4</sub> <sup>°</sup> (aq), CdHCO <sub>3</sub> <sup>+</sup>
Calcium	Ca <sup>2+</sup> , CaSO <sub>4</sub> <sup>°</sup> (aq), Ca-org	Ca <sup>2+</sup> , Ca SO <sub>4</sub> <sup>°</sup> (aq), CaHCO <sub>3</sub> <sup>+</sup>
Chromium(III)	CrOH <sup>2+</sup>	Cr(OH) <sub>4</sub> <sup>-</sup>
Chromium(VI)	CrO <sub>4</sub> <sup>2-</sup>	CrO <sub>4</sub> <sup>2-</sup>
Copper(II)	Cu-org, Cu <sup>2+</sup>	CuCO <sub>3</sub> <sup>°</sup> (aq), Cu-org, CuB(OH) <sub>4</sub> <sup>+</sup> , Cu[B(OH) <sub>4</sub> ] <sub>4</sub> <sup>°</sup> (aq)
Iron(II)	Fe <sup>2+</sup> , FeSO <sub>4</sub> <sup>°</sup> (aq), FeH <sub>2</sub> PO <sub>4</sub> <sup>+</sup>	FeCO <sub>3</sub> <sup>°</sup> (aq), Fe <sup>2+</sup> , FeHCO <sub>3</sub> <sup>+</sup> , FeSO <sub>4</sub> <sup>°</sup> (aq)
Iron(III)	FeOH <sup>2+</sup> , Fe(OH) <sub>3</sub> <sup>°</sup> (aq), Fe-org	Fe(OH) <sub>3</sub> <sup>°</sup> (aq), Fe-org
Lead	Pb <sup>2+</sup> , Pb-org, PbSO <sub>4</sub> <sup>°</sup> (aq), PbHCO <sub>3</sub> <sup>+</sup>	Pb <sup>2+</sup> , PbHCO <sub>3</sub> <sup>+</sup> , Pb-org, Pb(CO <sub>3</sub> ) <sub>2</sub> <sup>2-</sup> , PbOH <sup>+</sup>
Magnesium	Mg <sup>2+</sup> , MgSO <sub>4</sub> <sup>°</sup> (aq), Mg-org	Mg <sup>2+</sup> , MgSO <sub>4</sub> <sup>°</sup> (aq), MgCO <sub>3</sub> <sup>°</sup> (aq)
Manganese(II)	Mn <sup>2+</sup> , MnSO <sub>4</sub> <sup>°</sup> (aq), Mn-org	Mn <sup>2+</sup> , MnSO <sub>4</sub> <sup>°</sup> (aq), MnCO <sub>3</sub> <sup>°</sup> (aq), MnHCO <sub>3</sub> <sup>+</sup> , MnB(OH) <sub>4</sub> <sup>+</sup>
Molybdenum(VI)	H <sub>2</sub> MoO <sub>4</sub> <sup>°</sup> (aq), HMoO <sub>4</sub> <sup>-</sup>	HMoO <sub>4</sub> <sup>-</sup> , MoO <sub>4</sub> <sup>2-</sup>
Nickel	Ni <sup>2+</sup> , NiSO <sub>4</sub> <sup>°</sup> (aq), NiHCO <sub>3</sub> <sup>+</sup> , Ni-org	NiCO <sub>3</sub> <sup>°</sup> (aq), NiHCO <sub>3</sub> <sup>+</sup> , Ni <sup>2+</sup> , NiB(OH) <sub>4</sub> <sup>+</sup>
Potassium	K <sup>+</sup>	K <sup>+</sup> , KSO <sub>4</sub> <sup>-</sup>
Silicon	H <sub>4</sub> SiO <sub>4</sub> <sup>°</sup> (aq)	H <sub>4</sub> SiO <sub>4</sub> <sup>°</sup> (aq)
Sodium	Na <sup>+</sup>	Na <sup>+</sup> , NaHCO <sub>3</sub> <sup>°</sup> (aq), NaSO <sub>4</sub> <sup>-</sup>
Zinc	Zn <sup>2+</sup> , ZnSO <sub>4</sub> <sup>°</sup> (aq), Zn-org	ZnHCO <sub>3</sub> <sup>+</sup> , ZnCO <sub>3</sub> <sup>°</sup> (aq), Zn-org, Zn <sup>2+</sup> , ZnSO <sub>4</sub> <sup>°</sup> (aq), ZnB(OH) <sub>4</sub> <sup>+</sup>
<sup>1</sup> Complexes for each cation are listed in the order of their relative concentrations from greatest to lowest concentration.		
<sup>2</sup> Org = Organic complexes ( <i>e.g.</i> , fulvic acid complexes).		

Scientists will conduct geochemical studies with pure phases, such as goethite, quartz, or montmorillonite to work in well-defined systems. They may also choose not to work with actual groundwater, but instead work with a “synthesized groundwater,” such as a calcium chloride solution or a calcium chloride/sodium chloride solution. Again, the intent is to work in a chemically well-defined system with as few constituents as possible. Experiments conducted under simplified systems have provided information about the mechanisms by which solutes interact with solid surfaces (Sposito, 1984; Sposito, 1989), information that otherwise would not be possible to obtain from experiments conducted with natural heterogeneous soils and groundwater.

Ideally, for site-specific calculations, the transport modeler should use sorption values determined for site-specific materials at site-specific conditions. In the absence of such data, the modeler often selects a  $K_d$  value taken from the literature that was measured under similar conditions as existing at the study site. However, as discussed in Chapter 2 (Section 2.2.3), very subtle properties of the solid and aqueous phases can have a profound affect on a contaminants  $K_d$ . For example, only 1 percent (w/w) organic matter existing as surface coatings in a South Carolina surface soil completely masked the surface properties of the underlying minerals (Kaplan *et al.*, 1993). The organic coatings imposed a much greater sorption potential than would have been expected based on mineralogical considerations. Similarly, the surface properties of the soils just below these soils were entirely dominated by iron-oxide coatings (Seaman *et al.*, 1995). The effect of the iron-oxide coatings was to create a solid phase that was dominated by pH dependent charge surfaces. These subsurface soils adsorbed large amounts of anions because the pH was below the zero-point-of-charge [discussed in Chapter 2 (Section 2.2.3)] of the iron oxides, pH ~8. Subtle changes in the aqueous composition in a batch  $K_d$  test may also have a profound affect on the measured  $K_d$  value (Delegard and Barney, 1983). Thus, it is essential for the modeler selecting  $K_d$  values to recognize which solid and aqueous phase components have a strong affect on the sorption of the contaminant of interest. Identifying these important components is the subject of Volume II.

### **3.3.2 Field Variability**

The purpose of any soil sample is to obtain information about a particular soil. The sample itself is seldom, if ever, the entire soil mass in which one is interested. In statistics, this larger aggregate of material, in which we are ultimately interested, is called the “population.” Information from the sample is of interest only insofar as it yields information about the population, and the information may or may not be representative, depending on how the sample is selected.

The population itself may be large or small, or even a part of what the modeler considers a larger population. For contaminant transport modeling, the population is commonly defined by either stratigraphic units or soil texture. The justification supporting the use of these definitions is based both on practical and scientific considerations. Soil texture and stratigraphy can be easily and inexpensively determined from well-log data and the close correlation of a number of hydrological and chemical properties with soil textures is well documented (Petersen *et al.*, 1996). A some-

what better definition of soil populations would be the cation- or anion-exchange capacity of the soils. However, this option is appreciably more expensive and is valuable only for defining  $K_d$  populations. The soil texture data are also used for defining water flow populations.

The intensity with which a soil must be sampled to estimate with given accuracy some characteristic, such as  $K_d$  value, will depend on the magnitude of the variation within the soil population under consideration. The more heterogeneous the population, the more intense must be the sampling rate to attain a given precision. In general, although differences have been found to exist among lithographic units, considerable variation may be expected within the units for such characteristics as pH, phosphorous, potassium, sodium, conductivity, volume weight, permeability and porosity (Peterson and Calvin, 1986). In some instances, the variation within contiguous units is so great that it is not feasible to estimate differences between the units with any satisfactory degree of precision. For most characteristics, the variation, both within and among units, decreases, with increasing depth in the profile (Peterson and Calvin, 1986). Hence, subsurface environments generally need to be sampled less than surface soils to attain comparable accuracy (Mackay *et al.*, 1986; Warrick and Nielsen, 1980). Mackay *et al.* (1986) reported that a number of soil properties, including  $K_d$  values, changed more vertically than laterally.

### 3.3.3 The “Gravel Issue”

Because most  $K_d$  values are measured in laboratory studies, the sample size has an upper mass limit of about 100 g soil (and often 10 g with the increased emphasis of waste minimization and high disposal costs for laboratory wastes) in batch  $K_d$  measurements and several kilograms of soil in column studies. Both tests also have particle size limitations. The batch  $K_d$  is typically limited to the less than 2-mm size fraction (Appendix C, ASTM, 1987; EPA, 1991; Roy *et al.*, 1991). This size fraction was selected for a number of reasons that are both practical and scientific in nature. The less than 2-mm fraction has historically been defined as the soil fraction and the greater than 2-mm fraction as the rock fraction. The less than 2-mm fraction is also convenient for most standard glassware used in batch  $K_d$  tests (Figure 3.1). Another practical consideration is that greater uniformity of the soil sample and therefore of the measured  $K_d$  value can be achieved if the range of particle sizes used in the test is limited. Finally, the smallest fraction is the most chemically reactive fraction due to its high specific surface area ( $m^2/g$ ). The particle size used in column studies is also commonly limited to the less than 2-mm fraction. This size fraction was selected for similar reasons as for the batch studies and to compare results between the 2 common methods. However, Relyea (1982) indicated that the less than 2-mm size fraction should only be used in columns greater than 80 mm in diameter. He indicates that to avoid local velocity effects (*e.g.*, channeling or a radial velocity gradient), the column diameter should be at least 30 to 40 times the particle diameter of the solids used to pack the column.

The “gravel issue” is the problem that transport modelers face when converting laboratory-derived  $K_d$  values based on experiments conducted with the less than 2-mm fraction into values that can be used in systems containing particles greater than 2 mm in size. As mentioned above, the less than 2-mm fraction is the more chemically reactive fraction due primarily to its large

surface area. There are many subsurface soils dominated by cobbles, gravel, or boulders. To base the  $K_d$  values on the less than 2-mm size fraction, which may constitute less than 1 percent of the soil volume, would grossly overestimate the actual  $K_d$  of the aquifer. Including large soil particles in a  $K_d$  determination will increase the cost of laboratory equipment and perhaps more importantly will result in  $K_d$  values with large error terms because of the great variability of the particle size distribution in subsamples of a single soil.

Two general approaches have been proposed to address the “gravel issue.” The first is to assume that all particles greater than 2 mm have a  $K_d = 0$  ml/g. As an example, if 75 percent (w/w) of a formation is composed of particles greater than 2 mm and the  $K_d$  value of the less than 2-mm size fraction was 100 ml/g, then the  $K_d$  value used in the model would be 25 ml/g. Although the assumption underlying this approach is incorrect, the extent to which sorption occurs on these larger particles may be small. This approach is likely to yield a more accurate value in systems dominated by cobbles, gravel, and boulders.

The second approach is to normalize laboratory-derived  $K_d$  values by surface area. Thus, instead of having units of

$$\frac{\frac{\mu\text{g metal}}{\text{g sediment}}}{\frac{\mu\text{g metal}}{\text{ml solution}}} = \frac{\text{ml}}{\text{g}}, \quad (3.16)$$

the laboratory  $K_d$  value would have units of

$$\frac{\frac{\text{g metal}}{\text{m}^2 \text{ sediment}}}{\frac{\mu\text{g metal}}{\text{ml solution}}} = \frac{\text{ml}}{\text{m}^2}, \quad (3.17)$$

(Kaplan *et al.*, 1995b). Theoretically, this latter approach is more satisfying because it permits some sorption to occur on the >2-mm fraction and the extent of the sorption is proportional to the surface area. The underlying assumption in this approach is that the mineralogy is similar in the less than 2- and greater than 2-mm fractions and that the sorption processes occurring in the smaller fraction are similar to those that occur in the larger fraction. Because sorption is a surface area phenomena (Equation 3.16), as opposed to a weight phenomena (Equation 3.17), normalizing the data to surface area has logic, and is commonly done in soil (Sposito, 1989) and colloid chemistry (Alberty, 1987). The drawback to this approach is that an additional measurement is needed to calculate the newly defined  $K_d$  value in the laboratory. Specific surface area measurement is a rather common and simple procedure (Carter *et al.*, 1986). This approach

to the “gravel issue” also requires a means to convert available soil texture data, which are often available from well-hole logs or outcroppings of the formation, into surface area data.

### 3.3.4 The “Colloid Issue”

The “colloid issue,” as it pertains to measuring  $K_d$  values, is the problem experimentalists have in separating the aqueous from the solid phases during a laboratory batch  $K_d$  measurement (see Chapter 2). Typically centrifugation or filtration are used to accomplish this. If contaminants are sorbed to tiny particles that remain in suspension after the separation step, the experimenter will incorrectly assign the sorbed contaminant to the dissolved phase,  $C_i$  (Equation 3.2). This will result in underestimating the true  $K_d$  value. This is an especially important problem for contaminants that sorb strongly to solids, especially organic matter. Organic matter has a much lower density than clay (*i.e.*,  $\sim 1.05 \text{ g/cm}^3$  for organic matter versus  $\sim 2.6 \text{ g/cm}^3$  clays) and therefore the common centrifugation protocol may not be sufficient to separate the phases. Also, organic matter may exist as extremely small particles, or molecules,  $\sim 0.005 \mu\text{m}$  in diameter. Thus, when a great deal of organic matter is present in a soil, or when only a trace amount of organic matter has a profound affect on the measured  $K_d$ , additional precautions must be followed (Gschwend and Wu, 1985). For example, Gschwend and Wu (1985) reported that they were able to increase the partitioning coefficient, which is related to the  $K_d$  term (see Section 3.2.3), of polychlorinated biphenyl by 3 orders of magnitude by very carefully removing unsettled organic particles from suspension.

Using a centrifuge to make the solid and solution phase separations can also result in the formation of a very thin zone at the liquid surface where surface tension holds fine-grained particles at the top of the solution. The experimentalist should look for such problems and avoid sampling the surface of the clarified liquid. When pipets are used to remove supernatant solution, the pipet should be inserted sufficient distance below the surface to avoid drawing in suspended particles, but to a distance where the pipet tip is above the settled solids-liquid interface to avoid drawing in previously settled fines.

For these reasons, many experimentalists prefer to filter the supernatant solution after centrifugation. Filtration does have its problems, however. Filtering a small volume of supernatant solution can bias the contaminant’s concentration if the filter membrane adsorbs solute species. The type of filter membrane used effects the potential for adsorption. In our experience polyethylene or other plastic-based filter membranes are more inert than cellulosic-based membranes. Filter membranes can also be “pre-treated” with the supernatant solution by discarding the first aliquot and filtering a second aliquot that is saved for analysis. If the filter membrane does adsorb the analyte of interest, the amount adsorbed usually rapidly diminishes as the volume of solution filtered increases. Thus discarding the first aliquot of filtered solution and using subsequent aliquots for analysis lowers the chances of biasing final  $K_d$  values.

Another problem associated with colloids, is that the traditional 2-phase solute transport model does not account for contaminants moving in association with mobile colloids. This subject is

discussed in Chapter 2 (Section 2.5.1). Briefly, contaminants with a high affinity for sorbing to rock or vadose zone soils are assumed to be retarded relative to the rate of groundwater flow. However, an increasing body of evidence indicates that under some subsurface conditions, components of the solid phase may exist as colloids that may be transported with the flowing water. Association of contaminants with this additional mobile phase may enhance not only the amount of the contaminant that is transported, but also the rate of contaminant transport. Most current approaches to predicting contaminant transport ignore this mechanism not because it is obscure or the mathematical algorithms have not been developed (Corapcioglu and Kim, 1995; Mills *et al.*, 1991), but because little information is available on the occurrence, the mineralogical properties, the physicochemical properties, or the conditions conducive to the generation of mobile colloids. There have been numerous examples in which mobile colloids have been implicated as the vector responsible for enhanced transport (Kaplan *et al.*, 1994a,b; Kaplan *et al.*, 1995a; reviewed by McCarthy and Degueudre, 1993).

### 3.3.5 Particle Concentration Effect

Many investigators have observed that  $K_d$  values determined in the laboratory often exhibit a dependence with respect to the ratio of solid to solution used in the measurements. As recently discussed by Oscarson and Hume (1998), this dependence is puzzling. From a theoretical perspective, the  $K_d$  value should not depend on the solid-to-solution ratio, because the definition of the  $K_d$  model (see Equation 2.20) normalizes the ratio of the solute sorbed to the solid to the solute concentration left in solution based on the mass of solid and solution used for the measurement. Thus the  $K_d$  has units of volume/mass, such as typically ml/g.

Investigators have often found that  $K_d$  values measured for many contaminants for a given soil-groundwater system decrease as the solid-to-solution ratio increases. For example, this particle concentration effect on  $K_d$  values has been observed by O'Connor and Connolly (1980), Oscarson and Hume (1998), Honeyman and Santschi (1988), Meier *et al.* (1987), and others. The same trend with respect to particle concentration has also been observed for  $K_d$  values for organic contaminants [*e.g.*, see Gschwend and Wu (1985) and Voice *et al.* (1983)].

Investigators have offered several explanations for the observed dependency. These explanations can be categorized into two groups: (1) “real” physical/chemical processes, and (2) experimental artifacts. One rationalization offered in the “real” category is that the particle concentration effect is thought to be caused by particle-particle interactions. In systems with higher solids content, these interactions are perhaps physically blocking some adsorption sites from the adsorbing solutes and thus causing decreased adsorption, or creating electrostatic interferences such that the electrical surface charges on the closely packed particles diminish attractions between the adsorbing solutes and surfaces of individual grains. In terms of physical effects, individual particles in a slurry having a high solid-to-solution ratio may have a greater tendency to coagulate and flocculate into larger particles that have less available surface adsorption sites than individual grains and thus can adsorb less adsorbate. This phenomenon is likely exacerbated by diffusion processes that in short-term laboratory measurements, do not allow sufficient time for

the adsorbate to diffuse to the internal surface adsorption sites. The net effect is a  $K_d$  measurement with a lower value when a high solid-to-solution ratio is present, because not enough time was allocated for the water/soil system to reach a final equilibrium state. Thus there are possible experimental artifacts even within the context of this “real” process explanation.

Plausible experimental artifacts also include less efficient separation of the solid phase from high solids-content slurries, such that more colloidal size particles laden with adsorbate remain in the solution phase and the associated adsorbate gets included in the analysis of the solution phase. Complexing agents may desorb and/or dissolve from the solids, and in turn compete with the adsorbate for the available sorption surface sites. Soluble organic carbon is a common example of this process. Such effects increase when higher solid contents are used. Other artifacts include changes in the aqueous system that are caused by mass transfer from the larger quantity of solids but are not recorded during these measurements. Another consideration in the category of possible experimental artifacts for the solid-to-solution effect is improper data reduction. McKinley and Jenne (1991) suggest that the so-called particle concentration effect often goes away when adsorption data are replotted as adsorption isotherms, where the mass of solute adsorbed per mass of solid and the concentration of solute in the equilibrium solution are plotted on the y- and x-axes, respectively.

The explanations for the particle concentration (solid-to-solution ratio) effect are numerous and still rather perplexing [see summaries by Oscarson and Hume (1998) and Jenne (1998a)]. Jenne (1998a,b) includes valuable discussion on this “solids concentration effect.” He also presents some recommendations that should be followed when performing adsorption experiments and identifies several key issues that should be addressed by future adsorption research. One practical position that has been supported by EPRI (1991) is to conduct adsorption experiments as close as possible to the conditions that exist at the site where contaminant mobility is being simulated and assessed. In most cases, this recommendation would require that  $K_d$  values determined by flow-through column testing would be preferred over batch measurements conducted at low solid-to-solution ratios.

As noted above, it has been suggested that  $K_d$  values may decrease with increasing solid-to-solution ratios. If this is a real effect, application of  $K_d$  values based on a batch experiment conducted with a solid-to-solution ratio significantly less than those that would exist in the field would therefore overestimate the magnitude of contaminant sorption and underestimate the extent of contaminant migration.

### **3.4 Methods of Acquiring $K_d$ Values from the Literature for Screening Calculations**

#### ***3.4.1 $K_d$ Look-Up Table Approach: Issues Regarding Selection of $K_d$ Values from the Literature***

Clearly, the greatest limitation of using a  $K_d$  value to calculate a retardation term (Equations 3.8, 3.9, 3.10, and 3.11) is that it describes solute partitioning between the aqueous and solid phases

for only 1 set of environmental conditions.  $K_d$  values are known to vary greatly with only slight changes in the composition of the solid and aqueous phases and these conditions often vary greatly in 1 study site. For example, when the aqueous chemistry for a batch  $K_d$  measurement was varied, americium  $K_d$  values in a Hanford sediment ranged from 0.2 to 53 ml/g, greater than a 200-fold difference (Delegard and Barney, 1983). Additional variability in the americium  $K_d$  values were observed when slightly different Hanford sediments were used: 4.0 to 28.6 ml/g (Delegard and Barney, 1983). Similarly, Sheppard *et al.* (1976) measured americium  $K_d$  values ranging from 125 to 43,500 ml/g using identical aqueous phases but different soils.

An alternative approach to a constant  $K_d$  model is one in which the  $K_d$  value varies as a function of a select group of environmental conditions (Delegard and Barney, 1983; Routson and Serne, 1972; Streng and Peterson, 1989). The easiest variable  $K_d$  model to interface with a transport code is one based on a look-up table. For look-up tables, separate  $K_d$  values are assigned to a matrix of discrete categories defined by chemically important environmental parameters (Streng and Peterson, 1989; Whelan *et al.*, 1992). Streng and Peterson (1989) used 9 categories defined by soil pH and texture in the Multimedia Environmental Pollutant Assessment System (MEPAS) code. The 3 soil texture classes were <10 percent, 10 to 30 percent, >30 percent clay/organic matter/oxide content. The 3 pH classes were >9, 5 to 9, and <5. The 9 cells defined by the pH and soil texture classes contained literature-derived  $K_d$  values and where data was not available, estimated values were included in the table. The inorganic contaminants in the  $K_d$  look-up table were actinium, aluminum, americium, antimony, arsenic, asbestos, barium, beryllium, borate, cadmium, calcium hypochlorite, calcium oxide, carbon, cerium, chlorate, chromium (III), chromium (VI), cobalt, copper, curium, europium, fluoride, hydrogen fluoride, iodine, iron, krypton, lead, lead oxide, lithium hydroxide, lithium ion, magnesium, manganese, mercury, molybdenum, neptunium, nickel, niobium, nitrate, nitric acid, nitrogen dioxide, palladium, phosphate ion, phosphorus, plutonium, polonium, potassium hydroxide, potassium ion, protactinium, radium, ruthenium, samarium, selenium, silicate ion, silver, sodium ion, strontium, sulfate, sulphur, thallium, thorium, tin, tritium, uranium, vanadium, yttrium, zinc compounds, zinc, and zirconium.

For any literature-derived  $K_d$  value, it is essential to clearly understand the selection criteria and the logic used to estimate  $K_d$  values not found in the literature. For instance, Streng and Peterson (1989) reported a wide range of literature  $K_d$  values for several cells, typically greater than 10-fold and sometimes greater than a 100-fold difference between minimum and maximum values. The values included in the MEPAS look-up table were the minimum values found in the literature. They justified this criteria because they wanted to build conservatism into the code. Conservatism is traditional when addressing the extent of contaminant migration and associated health effects, but may be erroneous if the modeling calculations are being used to address remediation options, such as pump-and-treat remediation. Conservatism for remediation calculations would tend to error on the side of under estimating the extent of contaminant desorption that would occur in the aquifer once pump-and-treat of soil flushing treatments commenced. Such an estimate would provide an upper limit to time, money, and work required to extract a contaminant from a soil. This would be accomplished by selecting a  $K_d$  from the



upper range of literature  $K_d$  values. Thus, the  $K_d$  values in MEPAS would not provide a conservative estimate for clean-up efforts .

Other important issues regarding the use of literature-derived  $K_d$  values are illustrated in Table 3.2. In any  $K_d$  look-up table, a small number of ancillary parameters must be selected to define the cells. pH and soil texture were the ancillary parameters used in the MEPAS code. These are excellent general categories for a large number of contaminants, however, they are of only secondary importance to a large number of other contaminants. For example, the amount of vermiculite, which is a 2:1 layer silicate mineral common in the United States, especially in the west and mid-west, is arguable the single most important ancillary parameter affecting cesium sorption (Douglas, 1989). Redox state is another example of an ancillary parameter that is extremely important relative to affecting the removal from redox-sensitive contaminants solution [this is actually a precipitation process and not an adsorption phenomena (Ames and Rai, 1978; Rai and Zachara, 1984; Sposito, 1989)]. Some important redox sensitive contaminants include arsenic, chromium, molybdenum, neptunium, plutonium, selenium, technetium, and uranium. The  $K_d$  values of uranium in the 9 MEPAS categories range from 0 to 500 ml/g (Table 3.2).

**Table 3.2.** Example of a  $K_d$  (ml/g) look-up table for uranium, uranium(VI), and uranium(IV).

Material	pH								
	9			5 - 9			≤ 5		
Fines <sup>1</sup> (%)	<10	10-30	>30	<10	10-30	>30	<10	10-30	>30
U <sup>2</sup>	0	5	50	0	50	500	0	5	50
U(IV) <sup>3</sup>	200	500	1,000	100	250	500	20	30	50
U(VI) <sup>3</sup>	0	1	2	1	2	5	2	5	20
<sup>1</sup> Fines (%) = sum of percentages of clay, organic matter, and hydrous-oxide in soil <sup>2</sup> Reference: Streng and Peterson (1989) <sup>3</sup> Authors' opinion based on values reported in Ames and Rai (1978), Ames and McGarrah (1980), Cloninger <i>et al.</i> (1980), Cloninger and Cole (1981), Serne and Relyea (1981), and Rai and Zachara. (1984).									

By including an additional ancillary parameter of oxidation state, appreciably greater accuracy can be assigned to  $K_d$  values. For U(VI), the 9 categories may be assigned  $K_d$  values in the range of 0 to 20 ml/g, whereas, as for U(IV), the 9 categories may be assigned  $K_d$  values in the range of 20 to 1,000 ml/g. In this example, oxidation state is obviously a more important ancillary parameter than soil texture and in systems with pH values greater than 5, oxidation state is more important

than pH. The reduced form of U, U(IV), has a much greater  $K_d$  value than U(VI) because the former is known to precipitate from solution. The rather low uranium  $K_d$  values reported by Streng and Peterson (1989) are somewhat misleading in that they represent, as mentioned above, minimum values identified in the literature. These values would be entirely inappropriate for modeling U(IV) transport. Thus, an important point to this discussion is that no single set of ancillary parameters, such as pH and soil texture, is universally appropriate for defining categories in  $K_d$  look-up tables for all contaminants. Instead, the ancillary parameters used in look-up tables must be based on the unique chemical properties of each contaminant.

An apparent inconsistency in Table 3.2 is that the minimum values selected by Streng and Peterson (1989) for the uranium data are greater than those for U(VI). This inconsistency is not due to differences in literature used to estimate these values. Instead it arises from differences in how  $K_d$  values are estimated for cells in which no data are available.<sup>1</sup> This illustrates another important reason for clearly understanding the criteria and process used in selecting data incorporated into a look-up table. Clearly, differences in the criteria and process used to select  $K_d$  values can result in appreciable different values included in a look-up table; in this example, as much as 3 orders of magnitude.

### 3.4.2 Parametric $K_d$ Approach

The parametric  $K_d$  approach is similar to that of the  $K_d$  look-up table approach in that it varies  $K_d$  values used in a transport model as a function of important ancillary parameters. It differs from the  $K_d$  look-up table in that it uses a regression equation to define the  $K_d$  values instead of using discrete categories. The  $K_d$  value in this model varies as a function of empirically derived relationships with aqueous and solid phase independent parameters. Thus, it has the distinct advantage over look-up tables of having a continuum of  $K_d$  values.

Factorial design experiments are most often used to determine the systematic change resulting from varying the independent variables (*e.g.*, pH, soil texture, and redox status) on the dependent variables (uranium  $K_d$ ) (Box and Behnken, 1960; Cochran and Cox, 1957; Davies, 1954; Plackett and Burman 1946). Statistical methods commonly used to derive quantitative predictor equations include standard linear or nonlinear regression (Snedecor and Cochran, 1967), stepwise regression

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<sup>1</sup> Streng and Peterson (1989) generated most of the values in the pH>9 categories by multiplying the  $K_d$  values from the pH 5 to 9 category by 0.1. A significant quantity of  $K_d$  values exist in the literature for the latter pH category. The “0.1 factor” was based on consistent, but flawed logic that metal contaminants are less likely to sorb because their cationic valence decreases by  $[M^{a+}(OH)_x]^{a-x}$ . It is now known that hydrolysis species adsorb as well as or better than free cations ( $M^{a+}$ ). Also many contaminants precipitate at higher pH values, giving the appearance of increased  $K_d$  values. There are a few exceptions in pH >9 systems:  $Zr(OH)_5$  species that may not adsorb as well as  $Zr^{4+}$ , and  $UO_2(CO_3)_2^{2-}$  and  $UO_2(CO_3)_3^{4-}$  species do not adsorb as well as the  $UO_2^{2+}$  and  $UO_2OH^+$  species. The  $CO_3^{2-}$  activity increases as pH increases so complexes get more important at elevated pH levels.

(Hollander and Wolfe, 1973), and adaptive-learning networks (Mucciardi *et al.*, 1979, 1980). All these techniques have been used to develop empirical relationships describing  $K_d$  values in terms of other variables (Delegard and Barney, 1983; Routson and Serne, 1972; Serne *et al.*, 1973; Routson *et al.*, 1981).

The empirical predictor equations commonly take the form of a nonlinear polynomial expression. For example, after evaluating solutions consisting of several sodium salts, organic chelates, and acids, Delegard and Barney (1983) came up with the following expression for an americium  $K_d$  value:

$$\text{Log } K_d (\text{Americium}) = 2.0 + 0.1[\text{NaOH}] - 26.8[\text{HEDTA}] + 153.4[\text{HEDTA}]^2 \quad (3.18)$$

where HEDTA is N-(2-hydroxyethyl) ethylenediaminetetraacetic acid. Numerous salts were found to have no significant effect on americium  $K_d$  values and therefore were not included in the expression. Delegard and Barney (1983) also evaluated higher exponential and logarithmic terms and determined that these terms did not improve the predictive capabilities of the expression (*i.e.*, the regression coefficients were not significant at  $P \leq 0.05$ ).

It is critical that parametric  $K_d$  equations, such as Equation 3.18, be used to calculate  $K_d$  values for systems within the range of the independent variables used to create the equation. In the case of Equation 3.18, the range of independent variables used to generate the model were selected to simulate a plume beneath the Hanford Site in Richland, Washington. Using Equation 3.18 to generate americium  $K_d$  values for a plume low in pH and Na concentrations would not be appropriate.

These types of statistical relationships are devoid of causality and therefore provide no certain information regarding the mechanism by which the contaminant partitioned to the solid phase, whether it be by adsorption, absorption, or precipitation. For example, the statistical analyses may suggest a very strong relationship between pH and the  $K_d$  term, when the actual sorption process may be controlled by iron oxide adsorption. Because pH and iron-oxide charge are covariates, a statistical relationship may suggest that sorption is due to pH, when in fact, suggesting that sorption is solely caused by pH.

The parametric  $K_d$  model is used in the transport equation, the code must also keep track of the current value of the independent variables (*e.g.*, [NaOH] and [HEDTA] for the examples described in Equation 3.18) at each point in space and time to continually update the concentration of the independent variables affecting the  $K_d$  value. Thus, the code must track many more parameters, and some numerical solving techniques (*e.g.*, closed-form analytical solutions) can no longer be used to perform the integration necessary to solve for concentration. Generally, computer codes that can accommodate the parametric  $K_d$  model use a chemical subroutine to update the  $K_d$  value used to determine the  $R_f$ , when called by the main transport code. The added complexity in solving the transport equation with the parametric  $K_d$  sorption model and its empirical nature may be the reasons this approach has been used sparingly.

### 3.4.3 Mechanistic Adsorption Models

Mechanistic models explicitly accommodate for the dependency of  $K_d$  values on contaminant concentration, competing ion concentration, variable surface charge on the adsorbent, and solute species solution distribution. Incorporating mechanistic, or semi-mechanistic, concepts into models is attempted because the models become more robust and, perhaps more importantly from the standpoint of regulators and the public, scientifically defensible. The complexity of installing these mechanistic adsorption models into existing transport codes is difficult to accomplish. Additionally, these models also require a more intense and costly data collection effort than will likely be available to the majority of contaminant transport modelers who are conducting screening calculations. Descriptions of the state of this science, with references to excellent review articles, are presented in Chapter 2 and 5. A review of the methodology associated with the determination of the constants for use in these mechanistic models, however, is beyond the scope of this project. A review of the mechanistic adsorption models contained in EPA's MINTEQA2 geochemical reaction code is also presented in Chapter 5.

### 3.5 Summary

The objective of this chapter is to describe methods used to measure  $K_d$  values. The advantages and disadvantages and the assumptions underlying each method were discussed, and are summarized in Table 3.3. A number of issues regarding the selection of  $K_d$  values from the literature for screening calculations are also addressed in this chapter. Specific issues discussed included the use of simple versus complex systems to measure  $K_d$  values, field variability, the "gravel issue," and the "colloid issue."

Clearly, the greatest limitation of using a  $K_d$  value to calculate a retardation term is that it is only applicable to a single set of environmental conditions. Consequently, researchers have generated  $K_d$  values that varies as a function of ancillary environmental parameters. They include the look-up table  $K_d$ , the parametric  $K_d$ , and the mechanistic  $K_d$ . Models generated for parametric  $K_d$  values have typically been for rather limited environmental conditions. Mechanistic  $K_d$  values are limited to uniform solid and aqueous systems with little application to the heterogeneous soils that exist in the natural environment. The easiest and the most common variable  $K_d$  model to interface with a transport code is the look-up table. No single set of ancillary parameters, such as pH and soil texture, is universally appropriate for defining categories in  $K_d$  look-up tables. Instead, the ancillary parameters must vary in accordance to the geochemistry of the contaminant. It is essential that the modeler fully understand the criteria and process used for selecting the values incorporated in such a table. Just as important is to understand the logic used to estimate  $K_d$  values not found in the literature. Differences in the criteria and process used to select  $K_d$  values can result in appreciable different  $K_d$  values.

It is incumbent upon the transport modeler to understand the strengths and weaknesses of the different  $K_d$  methods and perhaps more importantly the underlying assumption of the methods in order to properly select  $K_d$  values from the literature. The  $K_d$  values reported in the literature for

any given contaminant may vary by as much as *6 orders of magnitude*. An understanding of the important geochemical processes and knowledge of the important ancillary parameters affecting the sorption chemistry of the contaminant of interest is necessary for selecting appropriate  $K_d$  value(s) for contaminant transport modeling.

**Table 3.3.** Advantages, disadvantages, and assumptions of different methods used to determine  $K_d$  and the assumptions in applying these  $K_d$  values to contaminant transport models.

Methods for Determining $K_d$				
Batch <sup>1</sup>	<i>In-Situ</i> Field Batch	Flow-Through	Field Modeling	$K_{oc}$ <sup>2</sup>
Minimum Input Data <sup>3</sup>				
<ul style="list-style-type: none"> <li>• <math>M_{sed}</math></li> <li>• <math>C_i</math></li> <li>• <math>C_0</math></li> <li>• <math>V_w</math></li> </ul>	<ul style="list-style-type: none"> <li>• <math>C_i</math></li> <li>• <math>A_i</math> (or <math>q_i</math>)</li> </ul>	<ul style="list-style-type: none"> <li>• <math>C_o</math></li> <li>• <math>n</math>, <math>\theta</math>, or <math>n_e</math></li> <li>• <math>\rho_{particle}</math><sup>4</sup></li> <li>• <math>&gt;10</math> <math>C_{effluent}</math> data points</li> <li>• <math>C_o</math> tracer</li> <li>• Time</li> </ul>	<ul style="list-style-type: none"> <li>• <math>C_{release}</math></li> <li>• <math>C_{well}</math></li> <li>• Time</li> <li>• Distance</li> <li>• <math>v_w</math></li> <li>• <math>n</math>, <math>\theta</math>, or <math>n_e</math></li> <li>• Diffusion or dispersion coefficients</li> </ul>	<ul style="list-style-type: none"> <li>• <math>K_{oc}</math></li> <li>• <math>f_{oc}</math></li> </ul>
Advantages				
<ul style="list-style-type: none"> <li>• Inexpensive</li> <li>• Quick</li> </ul>	<ul style="list-style-type: none"> <li>• <i>In-situ</i> measurements</li> <li>• Equilibrium conditions</li> <li>• Aqueous and solid phases are precisely those of the modeled system</li> </ul>	<ul style="list-style-type: none"> <li>• Can measure sorption at field flow rates, <i>i.e.</i>, at non-steady state conditions</li> <li>• Can measure hydro-dynamic effects (<i>e.g.</i>, dispersion, colloidal transport, <i>etc.</i>) on <math>R_f</math>, and subsequently incorporate into <math>K_d</math> value</li> <li>• Can measure effects of chemical phenomena (<i>e.g.</i>, multiple species, reversibility, <i>etc.</i>) on <math>R_f</math> and <math>K_d</math> values.</li> </ul>	<ul style="list-style-type: none"> <li>• Derived <math>K_d</math> has the precise geochemical conditions and flow conditions of the study site</li> </ul>	<ul style="list-style-type: none"> <li>• Fairly accurate indirect method</li> <li>• Often can use look-up tables to get <math>K_{oc}</math> value</li> <li>• <math>f_{oc}</math> is an easy measurement</li> <li>• <math>K_{oc}</math> can be correlated with <math>K_{ow}</math> which has been measured for many different chemicals</li> </ul>

**Table 3.3.** Continued.

Methods for Determining $K_d$				
Batch <sup>1</sup>	<i>In-Situ</i> Field Batch	Flow-Through	Field Modeling	$K_{oc}$ <sup>2</sup>
Disadvantages				
<ul style="list-style-type: none"> <li>Provides estimate of chemical processes at equilibrium; flow conditions are not always at equilibrium</li> <li>Physics involved not considered</li> <li>Better mixing in batch than in nature</li> <li>Typically uses larger ratio of solution/soil than exist in nature</li> <li>Experiments measure <u>adsorption</u> instead of <u>desorption</u>, the dominant process in transport; desorption is typically much slower than adsorption</li> <li>Speciation of different forms not considered</li> </ul>	<ul style="list-style-type: none"> <li>Expensive to collect samples</li> <li>Commonly have high detection limits (undesirable) for measuring contaminant on solid phase (<math>A_s</math>, <math>q_s</math>)</li> <li>Site-specific data</li> <li>Cannot unequivocally differentiate between, adsorbed, precipitated, and structural constituents</li> </ul>	<ul style="list-style-type: none"> <li>Commonly flow-through system is not at equilibrium and therefore results cannot be applied to other flow conditions</li> <li>Directly measure <math>R_f</math>, then back out <math>K_d</math>; therefore must make assumptions about relation between <math>K_d</math> and <math>R_f</math><sup>5</sup></li> <li>Measured <math>K_d</math> values commonly vary with water velocity and column dimensions</li> <li>Requires relatively expensive equipment</li> <li>Requires a lot of time</li> <li>Complex experiment to conduct</li> <li>Data are commonly not well behaved, <i>i.e.</i>, asymmetric or peakless break-through curves</li> <li>Can investigate some secondary processes affecting contaminant transport, such as effects of unsaturated flow, colloid-facilitated contaminant transport, mobile vs immobile water phases</li> </ul>	<ul style="list-style-type: none"> <li><math>K_d</math> is truly site specific</li> <li><math>K_d</math> is transport model specific</li> <li>Need to make many assumptions about the water flow including uniform flow, direction, and path length that affect the calculated <math>K_d</math> value</li> <li>Measure <math>R_f</math>, then back out <math>K_d</math>; many assumptions go into relating <math>K_d</math> to <math>R_f</math></li> <li>May or may not be in equilibrium, therefore not a thermodynamic <math>K_d</math></li> <li><math>K_d</math> value greatly improves with more field data collected</li> <li>Calculations can be quite involved</li> </ul>	<ul style="list-style-type: none"> <li>For organic compounds only</li> <li>More hydrophobic the contaminant compound, more accurate the <math>K_d</math>; vice versa with hydrophilic compounds</li> </ul>

**Table 3.3.** Continued.

Methods for Determining $K_d$				
Batch <sup>1</sup>	<i>In-Situ</i> Field Batch	Flow-Through	Field Modeling	$K_{oc}$ <sup>2</sup>
Assumptions in Calculating $K_d$				
<ul style="list-style-type: none"> <li>• Adsorption rate = desorption rate</li> <li>• Only 1 type of surface adsorption site, A</li> <li>• Only 1 type of aqueous dissolved species, <math>C_i</math></li> <li>• <math>A \gg A_i</math></li> <li>• Activity of <math>A_i = 1</math></li> <li>• Equilibrium has been achieved during mixing period</li> <li>• No adsorbate on suspended colloids</li> <li>• No precipitation of adsorbate due to <math>C_0</math> concentration exceeding solubility</li> </ul>	<ul style="list-style-type: none"> <li>• Same as for batch <math>K_d</math></li> <li>• Measurement of adsorbed contaminant, <math>A_i (q_i)</math>, can differentiate between adsorbed, precipitated, and structural constituents</li> </ul>	<ul style="list-style-type: none"> <li>• Must assume a relationship between <math>R_f</math> and <math>K_d</math><sup>5</sup></li> <li>• Water flow and dispersion coefficient is constant</li> </ul>	<ul style="list-style-type: none"> <li>• Must assume a relationship between <math>R_f</math> and <math>K_d</math></li> <li>• Know <math>n_e</math> or <math>n</math></li> <li>• Must know the flow path and velocity of plume</li> <li>• Sorption is uniform in the study size</li> </ul>	<ul style="list-style-type: none"> <li>• Same as for laboratory batch <math>K_d</math></li> <li>• Organic contaminant sorbs (partition) only to organic matter in soil, no sorption occurs to inorganic phases</li> </ul>



**Table 3.3.** Continued.

Methods for Determining $K_d$				
Batch <sup>1</sup>	<i>In-Situ</i> Field Batch	Flow-Through	Field Modeling	$K_{oc}$ <sup>2</sup>
Assumptions in Applying Measured $K_d$ to Transport Model				
<ul style="list-style-type: none"> <li>• Adsorption of solute is linear, <i>i.e.</i>, it is independent of <math>C_i</math></li> <li>• Adsorption of solute is reversible</li> <li>• Solute movement is slow enough that equilibrium conditions exist between the solute and soil</li> <li>• Geochemical conditions (presence and concentration of background electrolytes and solid phases) of batch experiment are identical to those in aquifer</li> <li>• Temperature and pressure conditions of batch experiment are identical to those in the aquifer</li> <li>• Mixing in aquifer is as thorough as in batch experiment</li> <li>• Difference between the soil/water ratio in the aquifer and batch experiment is not important to <math>K_d</math> value</li> </ul>	<ul style="list-style-type: none"> <li>• Same as for laboratory batch <math>K_d</math> (except fourth point not relevant to <i>in-situ</i> batch method)</li> </ul>	<ul style="list-style-type: none"> <li>• It is more common to enter the <math>R_f</math> value derived from experiment than the <math>K_d</math> value into transport code; consequently, do not need to make any assumptions about the relationship between <math>R_f</math> and <math>K_d</math></li> <li>• If <math>R_f</math> value from column experiment is entered into transport code and the flow conditions of the experiment are similar to those in the site being modeled, then no assumptions need to be made regarding affect of nonequilibrium conditions</li> </ul>	<ul style="list-style-type: none"> <li>• None</li> </ul>	<ul style="list-style-type: none"> <li>• Same as for laboratory batch <math>K_d</math></li> </ul>
<sup>1</sup> See Equation 3.4 <sup>2</sup> See Equation 3.13 <sup>3</sup> $A$ = Concentration of free or unoccupied surface adsorption site on a solid phase; $C_i$ = the total dissolved adsorbate concentration remaining in solution at equilibrium; $f_{oc}$ = fraction of soil that is organic carbon; $C_{release}$ = concentration of solute at time of release; $C_{well}$ = concentration of solute in monitoring well; $M_s$ = soil mass; $A_i$ = the concentration of adsorbate on the solid at equilibrium; $n$ = total porosity; $n_e$ = effective porosity; $V_w$ = solution volume; $\rho_b$ = bulk density; $\rho_{particle}$ = particle density; $\theta$ = water saturation. <sup>4</sup> $\rho_{particle}$ is used to calculate bulk density ( $\rho_b$ ); $\rho_b = [\rho_{particle} (1 - n)]$ . <sup>5</sup> See Equations 3.8, 3.9, 3.10, and 3.11.				